Supporting Information

Sea Cucumber-Inspired Autolytic Hydrogels Exhibiting Tunable High Mechanical Performances, Repairability, and Reusability

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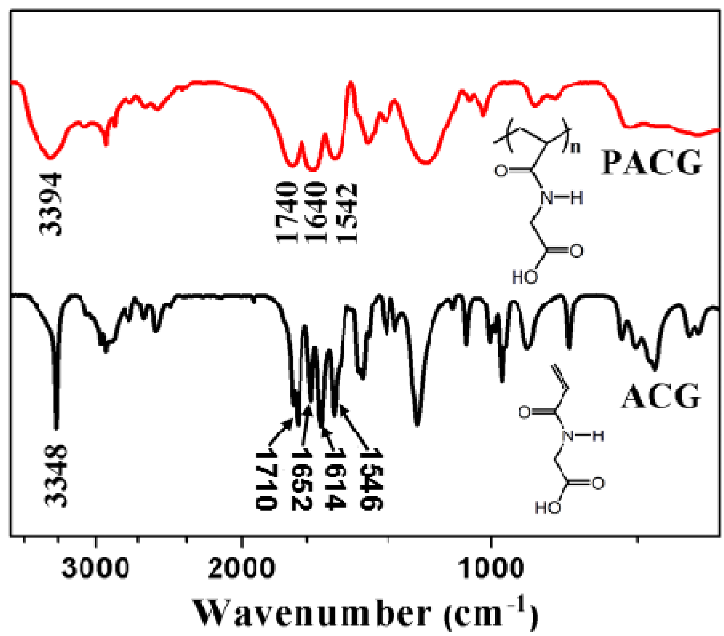

Figure S1. AIR-FTIR spectra of ACG and PACG.

In the spectrum of ACG, the peak appearing at 1614 cm^{-1} was attributed to acryloyl C=C stretching, and the peaks at 1652 and 1710 cm^{-1} were assigned to C=O stretching in amide and carboxyl groups, respectively; while signals from N–H bending and stretching appeared at 1546 and 3348cm^{-1} respectively.[1] The peak of acryloyl double bond of ACG monomer at 1614 cm^{-1} disappeared completely in the spectrum of PACG, indicating the occurrence of polymerization reaction, that is formation of hydrogels.

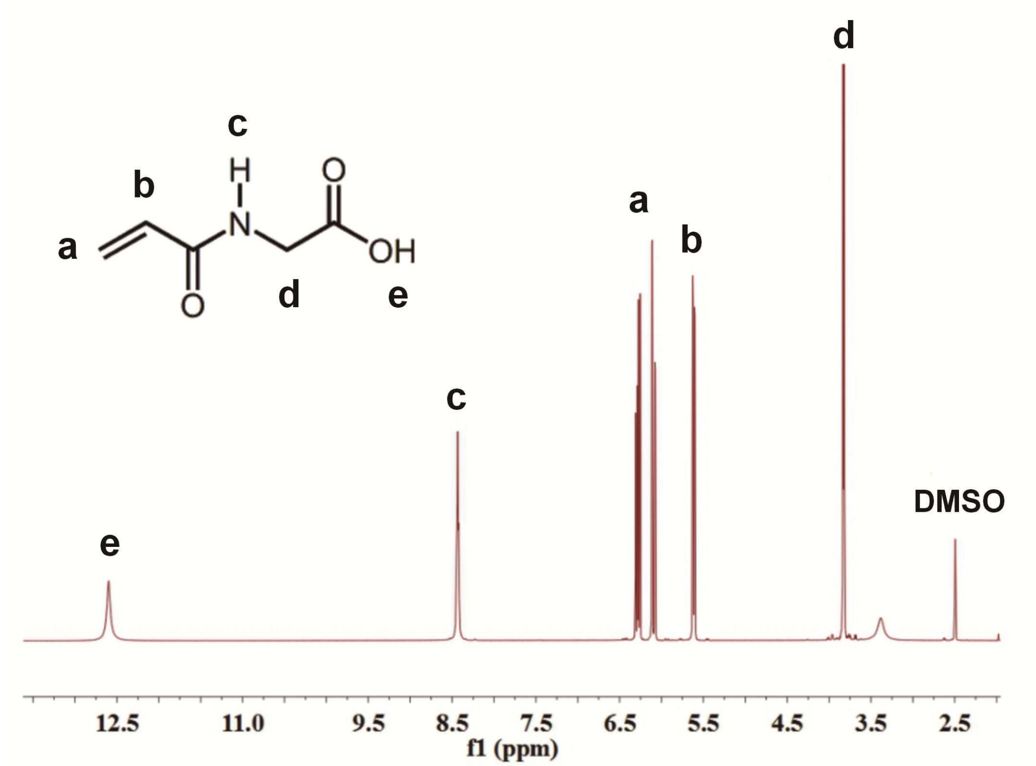

Figure S2. ^{1}H NMR spectrum of ACG in DMSO-d6.

Figure S2 shows ^{1}H NMR spectrum of ACG (400 MHz, DMSO-d6): 6.3 and 6.1 (C$\boldsymbol{H_2}$CHCONHCH$_2$COOH, 1H, s and 1H, s) (**a**), 5.6 (CH$_2$C**H**CONHCH$_2$COOH, 1H, s) (**b**), 8.4 (CH$_2$CHCON***H***CH$_2$COOH, 1H, s) (**c**), 3.8 (CH$_2$CHCONHC$\boldsymbol{H_2}$COOH, 1H, s) (**d**), 12.6 (CH$_2$CHCONHCH$_2$COO***H*,** 1H, s) (**e**).[2]

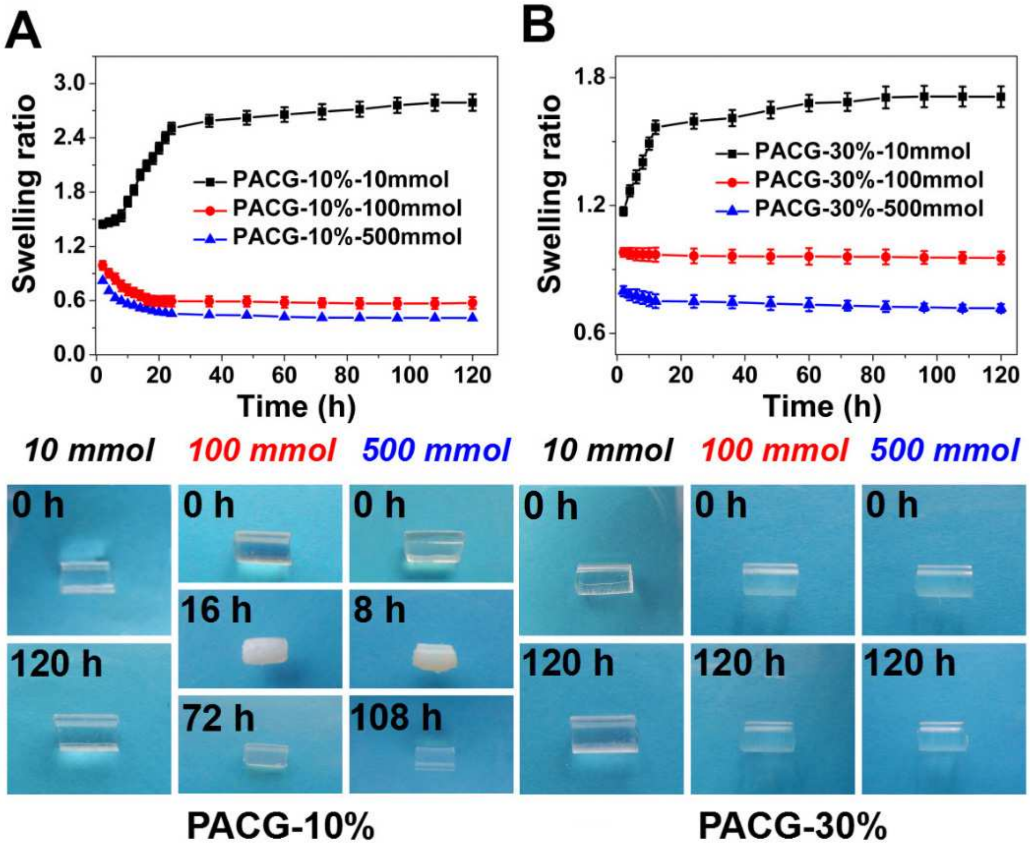

Figure S3. Swelling ratios of PACG-10% (A) and PACG-30% (B) hydrogels in different concentrations of calcium chloride solutions (10 mmol, 100 mmol, 500 mmol) as a function of time. The photographs from left to right represent the states of PACG-10% hydrogels immersed in 10 mmol, 100 mmol and 500 mmol calcium chloride solutions for different times, and PACG-30% hydrogels after soaking in 10 mmol, 100 mmol and 500 mmol calcium chloride solutions for 0 h and 120 h. The pH value of aqueous solution of the calcium chloride is slightly lower than that of deionized water (DIW, pH=6.7), but higher than $pKa_{-COOH.}$

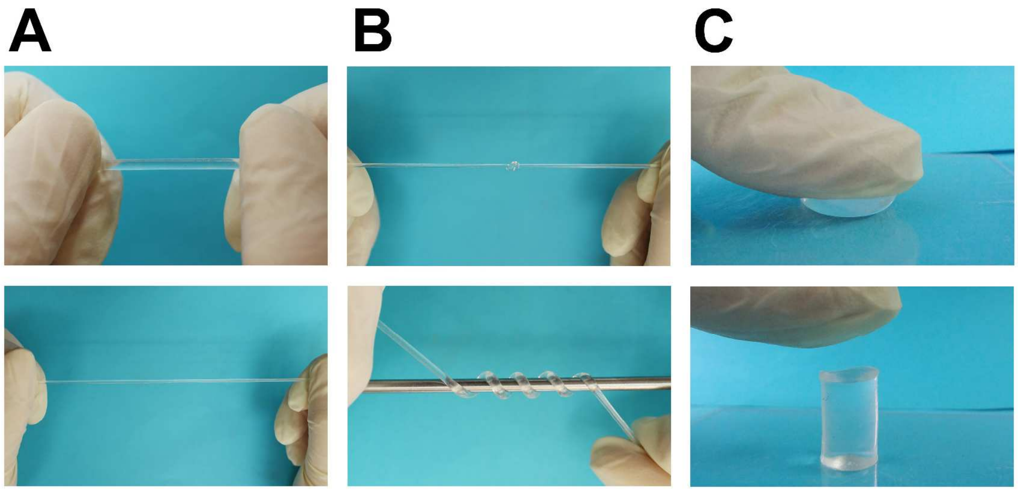

Figure S4. Photographs of PACG-20% hydrogel showing excellent mechanical performances. (A): large stretching; (B): knotting and twisting; (C): compression.

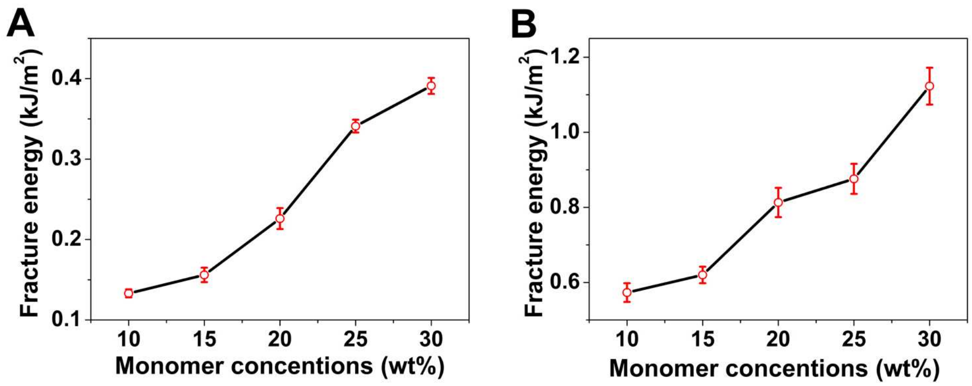

Figure S5. Fracture energies of PACG-X hydrogels prepared in deionized water (A) and PACG-X-Ca^{2+}-1 hydrogels prepared in Ca^{2+} solution (B).

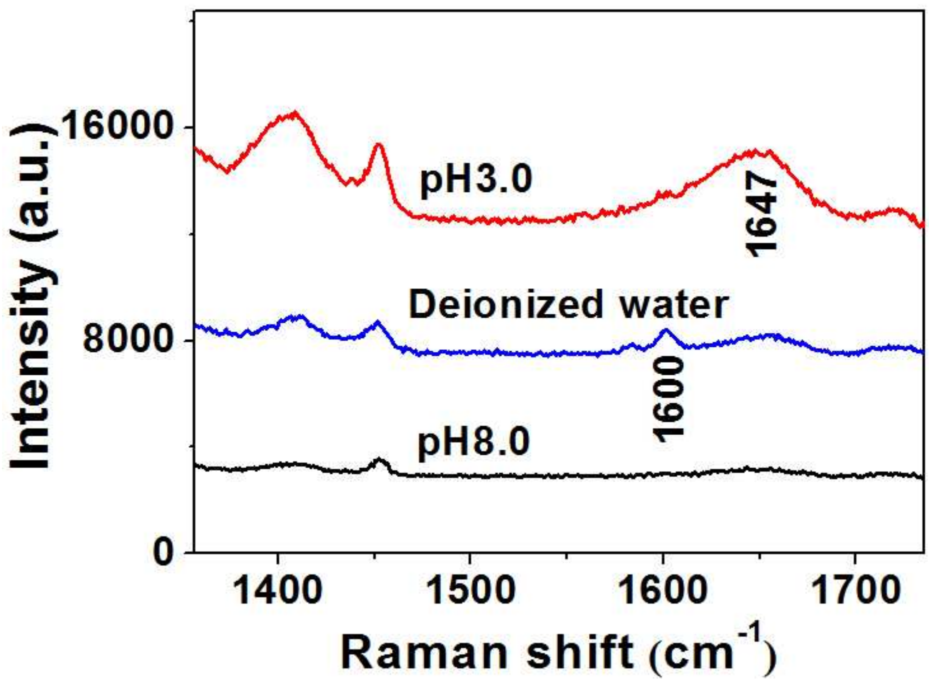

Figure S6. Raman spectra of PACG-20% hydrogel in different media.

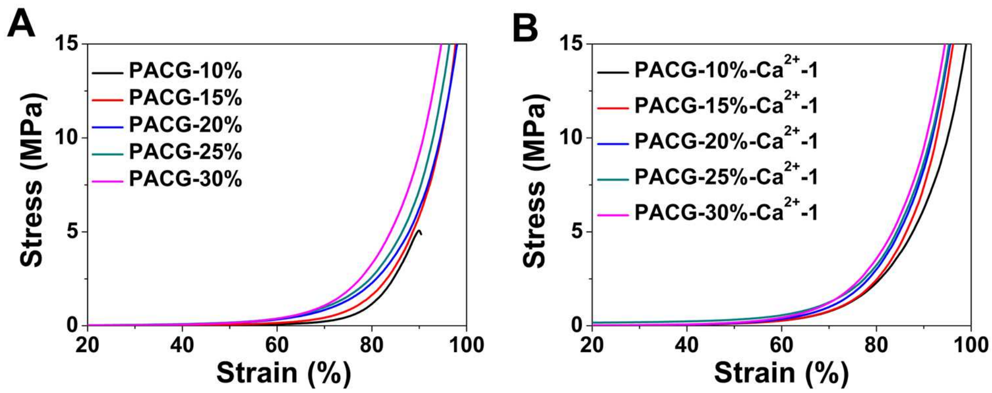

Figure S7. Compressive stress-strain curves of PACG-X hydrogels prepared in deionized water (A) and PACG-X-Ca^{2+}-1 hydrogels prepared in Ca^{2+} solution (1:1, Ca^{2+}/COO^{-}) (B) with different concentrations of initial monomers.

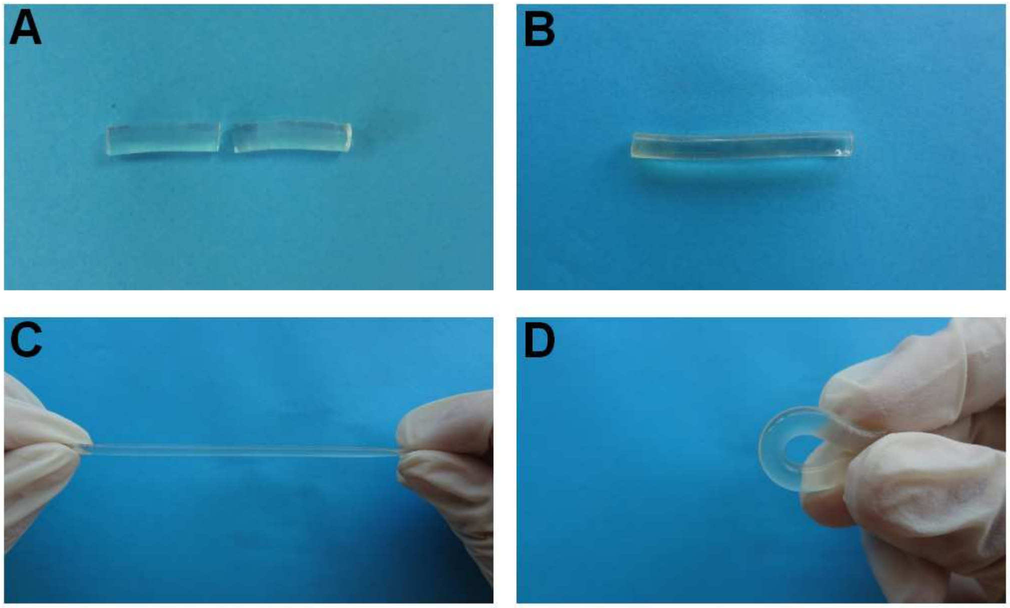

Figure S8. Photographs showing the self-healing of PACG-20% hydrogels. (A): a PACG-20% hydrogel was cut in the middle; (B): the two separated pieces were fused together at interface and completed healing when temperature was raised to 80 ºC and heated for 0.5 h; the healed hydrogel can withstand stretching (C) and bending (D).

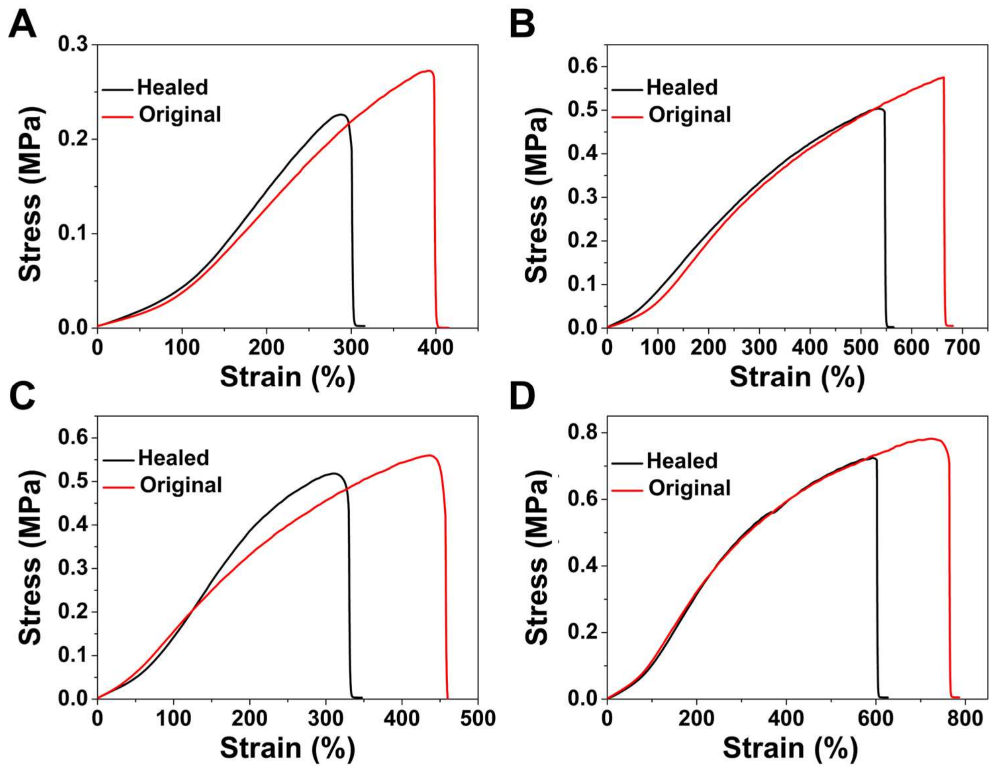

Figure S9. Tensile stress-strain curves of healed and heated original PACG-15% hydrogel at 75 ºC (A), healed and heated original PACG-15%-Ca^{2+}-1 hydrogel at 75 ºC (B), healed and heated original PACG-20% hydrogel at 80 ºC (C), healed and heated original PACG-20%-Ca^{2+}-1 hydrogel at 80 ºC (D). The original hydrogel was also subjected to the same heating treatment taking into account of the evaporation of water at an elevated temperature. All the samples were placed in a 75 ºC or 80 ºC water bath for 0.5 h. Note that there is only slight water loss in the repaired gels.

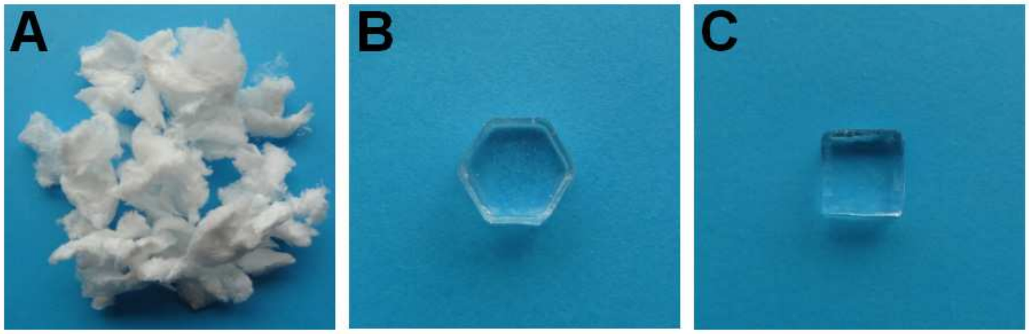

Figure S10. Photographs showing reusability of the PACG hydrogels. The lyophilized PACG (A) was dissolved in deionized water at 90 ºC to form 10 wt% aqueous solution, which was remolded into hexangular (B) and cubic (C) hydrogels.

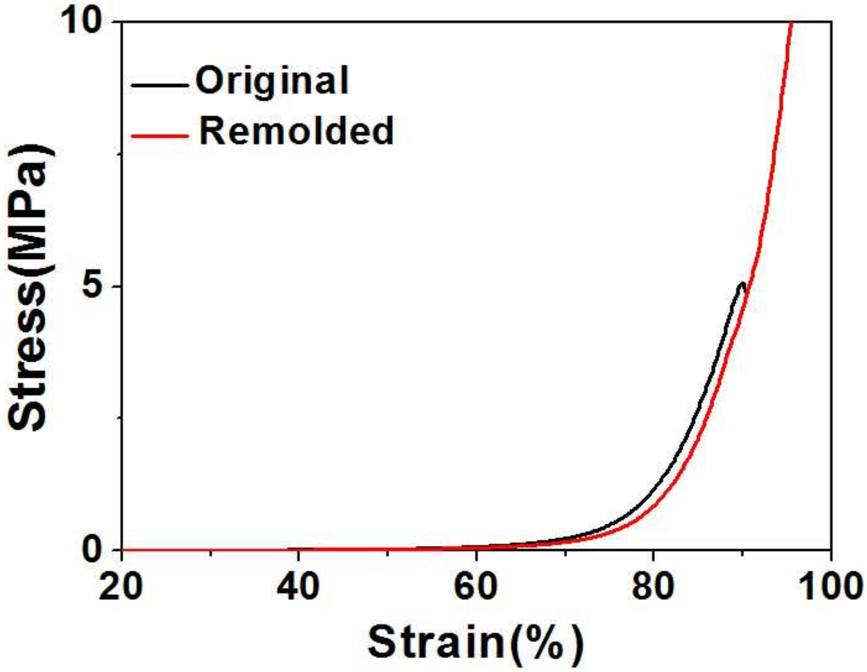

Figure S11. Compressive stress-strain curves of original PACG-10% and remolded PACG-10% hydrogels treated with pH3 solution.

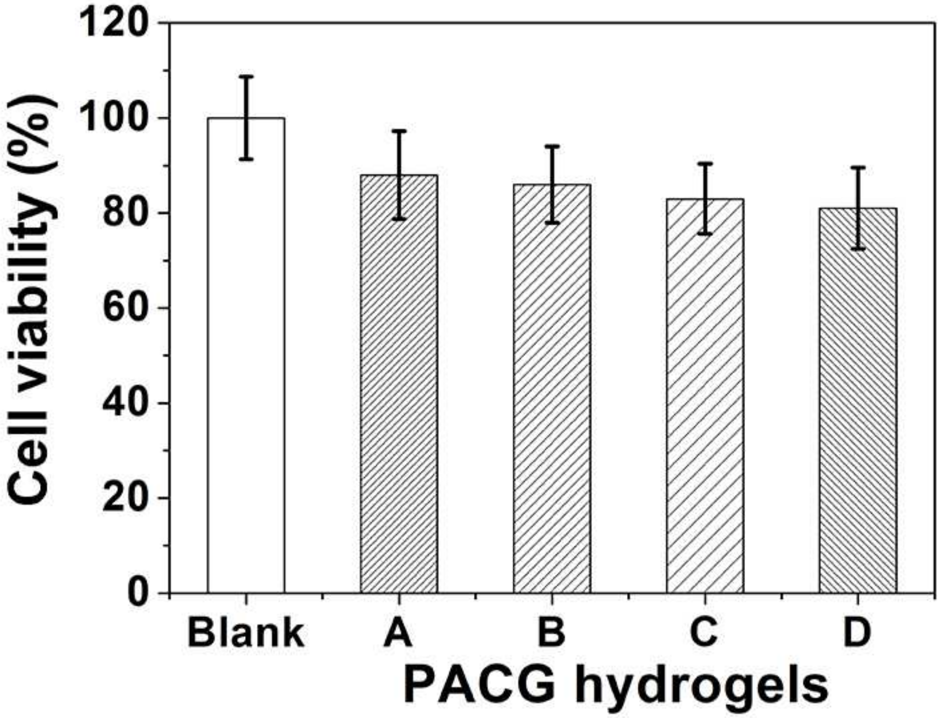

Figure S12. Cell viability of L929 cells co-cultured with the PACG-10% hydrogel (A), PACG-10%-Ca^{2+}-1 hydrogel (B), PACG-30% hydrogel (C), and PACG-30%-Ca^{2+}-1 hydrogel (D). Blank is the cells seeded on culture plate.

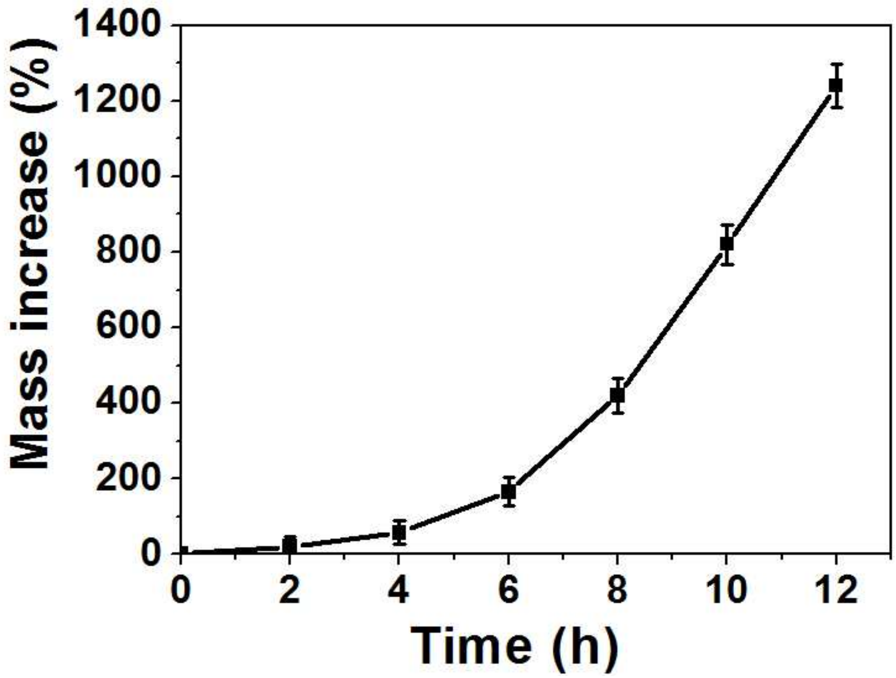

Figure S13. Mass increase of PACG-30% hydrogel resulting from water uptake as a function of subcutaneous implantation time.

Table S1. Mechanical properties of PACG hydrogels prepared with different monomer concentrations or Ca^{2+} contents.

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Compression strength at 90% strain (MPa)	Compression modulus (MPa)	Fracture energy (kJ/m^2)
PACG-10%	0.077 ± 0.003	175 ± 45	0.021 ± 0.006	4.891 ± 0.347	0.031 ± 0.002	0.133 ± 0.005
PACG-15%	0.208 ± 0.011	362 ± 32	0.035 ± 0.007	5.491 ± 0.636	0.067 ± 0.002	0.156 ± 0.009
PACG-20%	0.395 ± 0.015	436 ± 73	0.049 ± 0.013	6.118 ± 0.378	0.117 ± 0.006	0.226 ± 0.013
PACG-25%	0.815 ± 0.022	637 ± 71	0.153 ± 0.010	7.025 ± 0.560	0.211 ± 0.016	0.341 ± 0.033
PACG-30%	1.093 ± 0.029	1054 ± 56	0.171 ± 0.004	9.390 ± 0.092	0.223 ± 0.005	0.391 ± 0.006
PACG-10%-Ca^{2+}-1	0.189 ± 0.010	531 ± 61	0.023 ± 0.004	6.915 ± 0.350	0.044 ± 0.007	0.573 ± 0.025
PACG-15%-Ca^{2+}-1	0.452 ± 0.021	622 ± 72	0.055 ± 0.007	7.535 ± 0.820	0.092 ± 0.006	0.620 ± 0.022
PACG-20%-Ca^{2+}-1	0.528 ± 0.044	1022 ± 56	0.067 ± 0.004	8.330 ± 0.304	0.124 ± 0.002	0.813 ± 0.039
PACG-25%-Ca^{2+}-1	1.082 ± 0.077	1604 ± 63	0.123 ± 0.009	9.308 ± 0.657	0.178 ± 0.005	0.876 ± 0.04
PACG-30%-Ca^{2+}-1	1.251 ± 0.074	2257 ± 89	0.195 ± 0.007	10.820 ± 0.791	0.241 ± 0.003	1.023 ± 0.049

Table S2. Mechanical properties of PACG-20% hydrogels with varied Ca^{2+} contents.

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Compression strength at 90% strain (MPa)	Compression modulus (MPa)
PACG-20%-Ca^{2+}-0	0.395 ± 0.015	436 ± 73	0.049 ± 0.013	6.118 ± 0.378	0.107 ± 0.006
PACG-20%-Ca^{2+}-0.5	0.481 ± 0.011	774 ± 52	0.052 ± 0.003	7.467 ± 0.451	0.113 ± 0.03
PACG-20%-Ca^{2+}-1	0.528 ± 0.044	1022 ± 56	0.067 ± 0.004	8.330 ± 0.304	0.124 ± 0.002
PACG-20%-Ca^{2+}-1.5	0.977 ± 0.020	1288 ± 40	0.168 ± 0.014	8.871 ± 0.310	0.147 ± 0.006
PACG-20%-Ca^{2+}-2	0.713 ± 0.036	625 ± 76	0.151 ± 0.002	9.366 ± 0.208	0.185 ± 0.004

Table S3. Mechanical properties of PACG-20% hydrogels in different solvents.

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Compression strength at 90% strain (MPa)	Compression modulus (MPa)
PACG-20%	0.395 ± 0.015	436 ± 73	0.049 ± 0.013	6.118 ± 0.378	0.117 ± 0.006
PACG-20%-pH3.0	0.495 ± 0.064	450 ± 75	0.165 ± 0.003	8.367 ± 0.705	0.133 ± 0.006
PACG-20%-pH8.0	0.129 ± 0.036	617 ± 49	0.034 ± 0.002	5.62 ± 0.224	0.087 ± 0.003
PACG-20%-Ca-$^{2+}$-1-pH3.0	0.635 ± 0.072	1203 ± 60	0.065 ± 0.003	8.885 ± 0.304	0.151 ± 0.012
PACG-20%-Ca-$^{2+}$-1-pH8.0	0.210 ± 0.039	658 ± 53	0.046 ± 0.002	6.238 ± 0.372	0.095 ± 0.007

Movie S1. Escape behavior of PACG-10% hydrogel to imitate a sea cucumber.

References

(1) El-Sherbiny, I. M.; Lins, R. J.; Abdel-Bary, E. M.; Harding, D. R. K. Preparation, Characterization, Swelling and in Vitro Drug Release Behaviour of Poly[N-acryloylglycine-chitosan] Interpolymeric pH and Thermally-Responsive Hydrogels. *Eur Polym J.* **2005**, *41*, 2584–2591.

(2) Phadke, A., Zhang, C., Arman, B., Hsu, C. C., Mashelkar, R. A., Lele, A. K., Tauber, M. J., Arya, G. & Varghese, S. Rapid Self-Healing Hydrogels. *PNAS* **2012**, *12*, 4383-4388.